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Atanassov, Plamen K ; Linden, Anthony ; Heimgartner, Heinz

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**Selenium-Containing Heterocycles from Isoselenocyanates:
Synthesis of 1*H*-5-Selena-1,3,6-triazaaceanthrylene Derivatives**

by **Plamen K. Atanassov¹⁾**, **Anthony Linden** and **Heinz Heimgartner***

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¹⁾ Part of the planned Ph.D. thesis of *P.K.A.*, Universität Zürich.

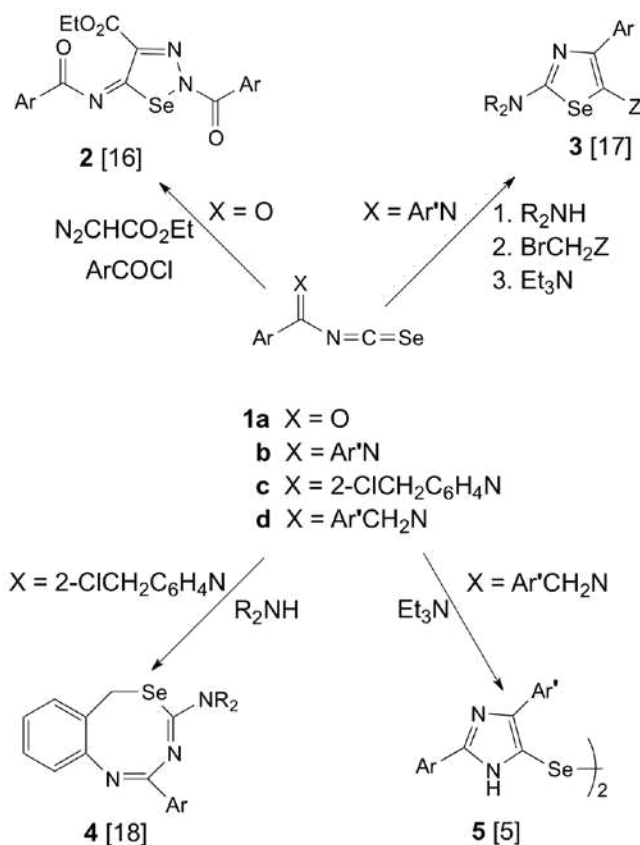
The reaction of aryl isoselenocyanates **8** with methyl 3-amino-4-chloro-1-ethylpyrrolo[3,2-*c*]quinoline-2-carboxylate (**6**) in boiling pyridine leads to tetracyclic selenaheterocycles of type **9** in high yield (*Scheme 3*). A reaction mechanism *via* an intermediate selenourea derivative **A** and cyclization *via* nucleophilic substitution of Cl by Se is proposed (*Schemes 3* and *5*). The reaction of **6** with (4-bromophenyl) isothiocyanate yields the analogous thiaheterocycle **12** (*Scheme 4*). The molecular structures of **9c** and **12** have been established by X-ray crystallography.

1. Introduction

The current interest in the chemistry of Se-containing compounds is well documented (*cf.* [1-4] and refs. cit. in [5]). A series of recent papers deals with biological activities and the pharmaceutical potential of Se-compounds (*e.g.* [6-10]). For example, some organo-selenium compounds are active as insecticides and microbicides [11], as prooxidants [12], and antimycobacterial agents [13]. Recently, the research group of *Koketsu* published some novel syntheses of selenaheterocycles [13-15].

Within our own research project, we have used aroyl isoselenocyanates **1a** and *N*-phenylbenzimidoyl isoselenocyanates **1b** as conveniently accessible, cheap and safe Se reagents for the preparation of 1,2,3-selenadiazole **2** [16] and 1,3-selenazole derivatives **3** [17], respectively (*Scheme 1*). In the case of **1c**, treatment with amines led to 6*H*-5,1,3-benzoselenadiazocines **4** [18], whereas the base-catalyzed cyclization of **1d** yielded bis(2,4-diarylimidazol-5-yl) diselenides **5** [5].

Scheme 1

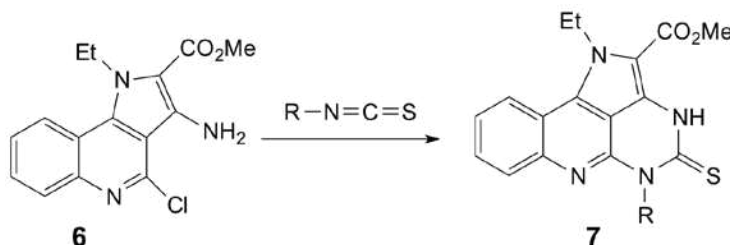


Although the chemistry of Se-containing compounds is often similar to that of the corresponding S analogues, some significant differences are also known, and because of the toxicity and instability of many Se compounds, the synthesis of Se heterocycles is much less developed. Therefore, new approaches by using more stable, less toxic, and easily accessible Se reagents are of high interest. For this reason, we have investigated reactions of aryl isoselenocyanates as starting materials for the preparation of selenaheterocycles.

In the present paper, we report the results of the reaction of aryl isoselenocyanates with methyl 3-amino-4-chloro-1-ethylpyrrolo[3,2-*c*]quinoline-2-carboxylate (**6**). The latter was used recently by *Mekheimer* to prepare fused tri- and tetracyclic quinoline derivatives [19]. Among several transformations, he described the reaction with phenyl and allyl isothiocyanate, which

gave – according to his interpretation – the corresponding 5-substituted methyl 1-ethyl-4-thioxo-3(4*H*)-1,3,5,6-tetraaza-aceanthrylene-2-carboxylate **7** (*Scheme 2*).

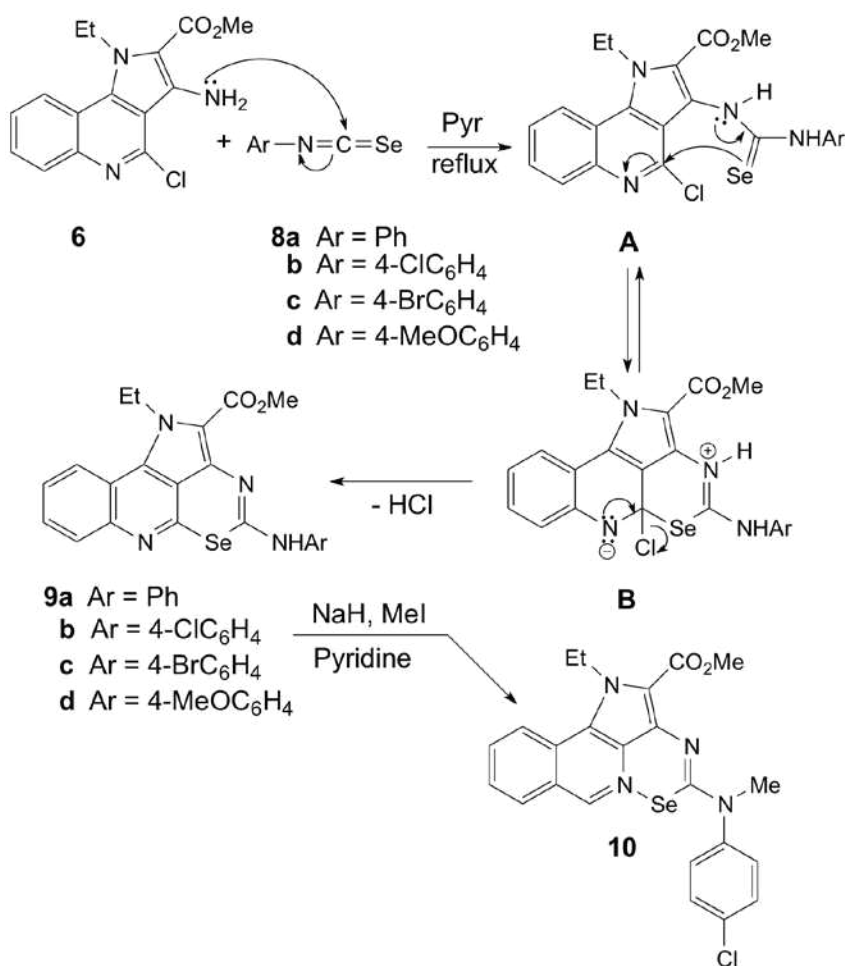
Scheme 2



2. Results and Discussion

To a solution of **6** in anhydrous pyridine, *ca.* 1.1 equiv. of the freshly prepared aryl isoselenocyanate **8** was added, and the mixture was heated under reflux for 5 h. After evaporation of the solvent, trituration of the residue with MeOH, and recrystallization, the corresponding yellowish crystalline product **9** was obtained (*Scheme 3*). According to the CI-MS and elemental analyses, these products were formed by addition of **6** and **8** and elimination of HCl. The IR spectra (KBr) showed absorptions at 3274-3244 and 1714-1692 cm⁻¹ for NH and the ester C=O group, and the corresponding signals appeared at 10.40-10.06 and 162.8-161.4 ppm in the ¹H- and ¹³C-NMR spectra. Other characteristic signals were present for the EtN and the MeO groups as well as for the C-atoms of the polycyclic skeleton in the aromatic region.

Scheme 3



As we expected that the formed products were Se analogues of **7** (Scheme 2), we tried to form the corresponding diselenides by oxidation (*cf.* [5]), but all attempts failed. Furthermore, methylation of **9b** by treatment with NaH and MeI gave a product **10**, which was not a methylseleno derivative. The Me absorption at 3.63 ppm (¹H-NMR) clearly shows that **10** is an N-methyl derivative.

In the case of the 4-bromophenyl derivative **9c**, single crystals were obtained from DMF, and the 1*H*-5-selena-1,3,6-triazaaceanthrylene structure of the molecule was established by X-ray crystallography (Fig. 1).

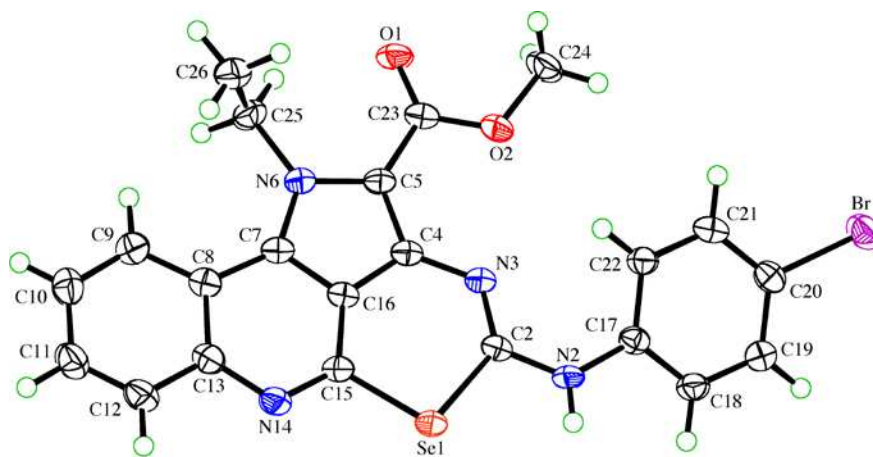


Fig. 1. ORTEP-Plot [20] of the molecular structure of **9c** (arbitrary numbering of atoms; 50% probability ellipsoids)

The tetracyclic ring system of **9c** is almost planar, and the ester group is coplanar with the ring system. The 4-bromophenyl ring at N(2) is twisted out of the heterocyclic plane by *ca.* 23° (torsion angles C(2)-N(2)-C(17)-C(18) -158.5(3)°, C(2)-N(2)-C(17)-C(22) 23.9(4)°). The Et group at N(6) is almost orthogonal to the ring skeleton (C(5)-N(6)-C(25)-C(26) -96.5(3)°). The NH group forms an intermolecular H-bond with the O-atom of the ester C=O group of a neighboring molecule, thereby linking the molecules into infinite chains which run in the [101] direction and have a graph set motif [21] of C(8).

A reaction mechanism for the formation of **9** is proposed in *Scheme 3*. Nucleophilic addition of the NH₂ group of **6** to the isoselenocyanate **8** leads to the selenourea derivative **A**. The new selenaheterocycle is formed by nucleophilic substitution of Cl of the β-chloroquinoline residue *via* attack of the Se atom, where **B** is an intermediate. As the reaction is carried out in pyridine, a base-catalysis of the ring closure is likely.

Because of the discrepancy between the reported reaction of **6** with isothiocyanates (*Scheme 2*) and the reaction with isoselenocyanates (*Scheme 3*), we also carried out a reaction with an aryl isothiocyanate. Treatment of **6** with (4-bromophenyl) isothiocyanate in pyridine at room temperature gave **12** in 64% yield (*Scheme 4*). According to the ^1H - and ^{13}C -NMR spectra in (D_7)DMF, there are two tautomeric forms **12** and **12'** present in a ratio of *ca.* 2:1. Crystals suitable for X-ray crystallography were obtained from DMSO (*Fig. 2*). The molecular structure of **12** is very similar to that of the corresponding Se analogue **9c**. The main difference is that the 4-bromophenyl ring at N(2) is almost coplanar with the heterocyclic ring system (torsion angles C(2)-N(2)-C(17)-C(18) $-177.0(2)^\circ$, C(2)-N(2)-C(17)-C(22) $2.8(3)^\circ$). The asymmetric unit contains one molecule of **12** plus one molecule of DMSO. The NH group forms an intermolecular H-bond with the O-atom of a neighboring DMSO molecule. This interaction does not form an extended network and has a graph set motif of D.

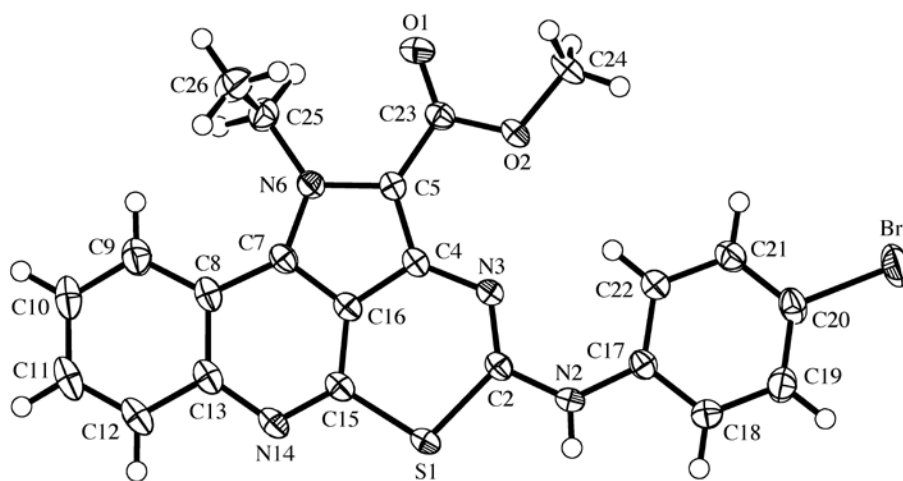
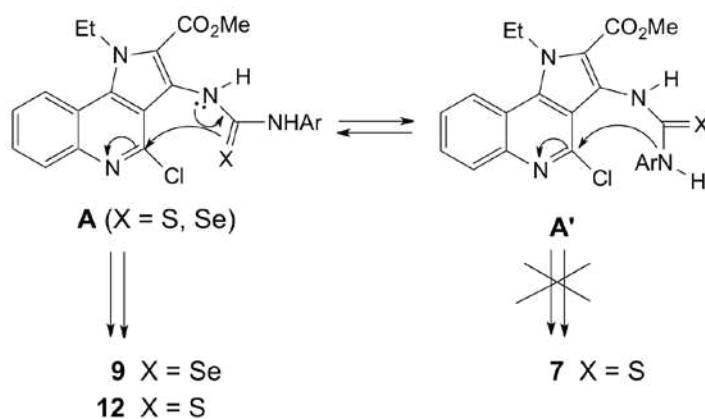


Fig. 2. ORTEP-Plot [20] of the molecular structure of **12** (arbitrary numbering of atoms; 50% probability ellipsoids)

In conclusion, we have shown that the reactions of **6** with aryl isoseleno- and isothiocyanates proceed in a consistent manner leading to the fused tetracyclic ring systems **9** and **12**, respectively. In both cases, the ring closure of the intermediate urea derivative of type **A** takes place by the nucleophilic attack of the Se and S atom (*Scheme 5*). The alternative cyclization *via* the N-atom of the urea derivatives, which was postulated to lead to the heterocycles of type **7** [19], was not observed. Therefore, the structures proposed in [19] have to be revised.

Scheme 5



We thank the analytical units of our institute for spectra and analyses. Financial support of this work by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

Experimental Part

1. *General*. See [16].

2. *Starting materials.* The aryl isoselenocyanates **8a** – **d** were prepared according to the protocol described in [22]. To a stirred soln. of the corresponding *N*-arylformamide (40 mmol) in abs. toluene (100 ml) in an ice bath were added Et₃N (16.2 g, 160 mmol) and Se black powder. Then, phosgene (30 g of a 20% soln. in toluene, 60 mmol) was added slowly within 30 min. An exothermic reaction took place. After complete addition, the suspension was heated under reflux for 8 – 10 h (TLC control). The mixture was filtered and washed with several portions of toluene, the filtrate was concentrated and fractionated over SiO₂ using hexane as the eluent. *Phenyl Isoselenocyanate (8a)* [22]: 4.84 g (40 mmol) of *N*-phenylformamide. Yield: 3.24 g (45%). *(4-Chlorophenyl) Isoselenocyanate (8b)* [22]: 6.22 g (40 mmol) of *N*-(4-chlorophenyl)formamide. Yield: 4.77 g (55%). *(4-Bromophenyl) Isoselenocyanate (8c)*: 8.00 g (40 mmol) of *N*-(4-bromophenyl)formamide. Yield: 6.05 g (58%). *(4-Methoxyphenyl) Isoselenocyanate (8d)* [22]: 6.05 g (40 mmol) of *N*-(4-methoxyphenyl)formamide. Yield: 3.56 g (42%). *N*-(4-Chlorophenyl)- and *N*-(4-bromophenyl)formamide were prepared according to [23] by heating the corresponding aniline (20 mmol) in 95% formic acid under reflux for 30 min. After workup, the products were recrystallized from H₂O. *N*-(4-Methoxyphenyl)formamide was prepared according to [24]. After evaporation of the solvent, the residue was dissolved in AcOEt and the soln. was washed with 5% aq. NaHCO₃ and H₂O. The org. layer was dried (MgSO₄), the solvent evaporated, and the crude product was used without further purification. *Methyl 3-Amino-4-chloro-1-ethylpyrrolo[3,2-c]quinoline-2-carboxylate (6)* was synthesized following the protocol in [19]. Cream-colored crystals. M.p. 185 – 186° (acetone). IR: 3496_m, 3384_m, 3068_w, 3016_w, 2985_w, 2956_m, 2930_w, 1692_s, 1602_s, 1573_s, 1556_m, 1534_s, 1507_s, 1472_m, 1435_s, 1409_w, 1374_s, 1356_m, 1330_m, 1298_m, 1276_s, 1255_m, 1240_s, 1180_s, 1160_s, 1102_s. ¹H-NMR (500 MHz, (D₆)DMSO): 8.38 (*dd*, *J* = 8.4, 0.9, 1 arom. H); 7.93 (*dd*, *J* = 8.2, 1.3, 1 arom. H); 7.73 (*td*, *J* = 8.2, 1.3, 1 arom. H); 7.67

(*td*, $J = 8.4, 1.4, 1$ arom. H); 6.04 (*s*, NH_2); 4.84 (*q*, $J = 7.0$, CH_2); 3.90 (*s*, MeO); 1.47 (*t*, $J = 7.0$, MeCH_2). ^{13}C -NMR ((D_6)DMSO): 161.7 (*s*, CO); 145.1, 144.3, 137.4, 136.4, 116.9, 108.0, 106.8 (7*s*, 7 arom. C); 129.0, 128.8, 126.7, 122.6 (4*d*, 4 arom. CH); 51.1 (*q*, MeO); 42.0 (*t*, CH_2); 15.2 (*q*, MeCH_2). CI-MS: 304 (100, $[M+1]^+$). Anal. calc. for $\text{C}_{15}\text{H}_{14}\text{ClN}_3\text{O}_2$ (303.74): C 59.31, H 4.65, N 13.83; found C 59.15, H 4.63, N 13.84.

3. *Preparation of 1H-5-Selena-1,3,6-triazaaceanthrylene-2-carboxylates 9a – d. General Procedure.* To a soln. of **6** in anhydrous pyridine, the freshly prepared arylisoselenocyanate **8** was added under stirring at r.t. The mixture was heated under reflux for 5 h. After cooling, the solvent was evaporated i.v. and the remaining oily residue was triturated with MeOH. The resulting solid product was collected by filtration and purified by recrystallization from MeOH or CH_2Cl_2 /hexane.

Methyl 1-Ethyl-4-(phenylamino)-1H-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate (9a). From 0.5 g (1.64 mmol) of **6** and 0.33 g (1.81 mmol) of **8a**: Yield: 0.55 g (75.3%). Yellowish crystals. M.p. 256.1 – 257.0° (MeOH). IR: 3244*w*, 3191*w*, 3125*w*, 3047*m*, 3012*m*, 2974*m*, 2931*m*, 1714*s*, 1628*s*, 1590*s*, 1569*s*, 1557*s*, 1546*s*, 1496*s*, 1456*m*, 1438*s*, 1371*m*, 1354*m*, 1312*m*, 1295*m*, 1269*m*, 1244*m*, 1216*m*, 1199*m*, 1183*m*, 1163*m*, 1140*w*, 1111*s*. ^1H -NMR (500 MHz, (D_6)DMSO): 10.20 (*s*, NH); 8.33 (*d*, $J = 7.6$, 1 arom. H); 8.09 (*d*, $J = 8.0$, 2 arom. H); 7.91 (*dd*, $J = 8.2, 1.2$, 1 arom. H); 7.68 (*td*, $J = 8.1, 1.1$, 1 arom. H); 7.61 (*td*, $J = 8.3, 1.3$, 1 arom. H); 7.39 (*dd*, $J = 8.4, 7.4$, 2 arom. H); 7.08 (*t*, $J = 7.3$, 1 arom. H); 4.95 (*q*, $J = 7.0$, CH_2); 3.99 (*s*, MeO); 1.51 (*t*, $J = 7.0$, MeCH_2). ^{13}C -NMR ((D_6)DMSO): 161.4 (*s*, CO); 152.4, 147.6, 147.2, 140.4, 135.4, 131.1 (6*s*, 7 arom. C); 128.7, 128.6, 128.5, 125.9, 122.9, 122.5, 119.4 (7*d*, 9 arom. CH); 117.9, 105.0 (2*s*, 2 arom. C); 51.5 (*q*, MeO); 41.9 (*t*, CH_2); 15.4 (*q*, MeCH_2). CI-MS: 451 (100,

[*M*+1]⁺). Anal. calc. for C₂₂H₁₈N₄O₂Se (449.36)²): C 58.80, H 4.04, N 12.47; found: C 56.84, H 4.25, N 11.95.

Methyl 4-[(4-Chlorophenyl)amino]-1-ethyl-1H-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate (9b). From 0.4 g (1.31 mmol) of **6** and 0.31 g (1.42 mmol) of **8b**: Yield: 0.55 g (87.3%). Yellowish crystals. M.p. 271.0 – 272.1° (MeOH). IR: 3261_w, 3190_w, 3102_m, 3055_m, 2990_m, 2950_m, 1694_s, 1605_s, 1570_s, 1549_s, 1489_s, 1461_m, 1435_s, 1420_w, 1400_m, 1373_s, 1353_m, 1308_s, 1292_s, 1263_m, 1246_m, 1223_s, 1196_m, 1180_m, 1161_m, 1135_w, 1110_s, 1094_m. ¹H-NMR ((D₇)DMF): 10.62 (*s*, NH); 8.62 (*d*, *J* = 8.2, 1 arom. H); 8.50 (*d*, *J* = 8.8, 2 arom. H); 8.18 (*d*, *J* = 8.0, 1 arom. H); 7.95 – 7.82 (*m*, 2 arom. H); 7.71 (*d*, *J* = 8.8, 2 arom. H); 5.26 (*q*, *J* = 7.0, CH₂); 4.35 (*s*, MeO); 1.85 (*t*, MeCH₂, *J* = 7.0). ¹³C-NMR ((D₇)DMF): 162.8 (*s*, CO)³; 153.0, 148.5, 140.5, 132.0, 129.8, 129.3, 118.1 (7_s, 10 arom. C); 129.1, 127.5, 126.5, 123.4, 121.5, 119.0 (6_d, 8 arom. CH); 52.2 (*q*, MeO); 42.9 (*t*, CH₂); 15.9 (*q*, MeCH₂). CI-MS: 485 (100, [*M*+1]⁺). Anal. calc. for C₂₂H₁₇ClN₄O₂Se (483.81): C 54.62, H 3.54, N 11.58; found: C 53.88, H 3.65, N 11.41.

Methyl 4-[(4-Bromophenyl)amino]-1-ethyl-1H-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate (9c). From 0.6 g (1.97 mmol) of **6** and 0.56 g (2.14 mmol) of **8c**. Yield: 0.9 g (86.5%). Colorless crystals. M.p. 265 – 267° (MeOH), 266.8 – 267.0° (CH₂Cl₂/hexane). IR: 3274_m, 3186_m, 3099_m, 3050_m, 2989_m, 1694_s, 1606_s, 1586_s, 1570_s, 1546_s, 1487_s, 1461_m, 1435_m, 1395_m, 1374_m, 1354_w, 1309_s, 1294_s, 1264_m, 1246_m, 1223_s, 1197_m, 1181_m, 1160_m, 1135_w, 1111_m. ¹H-NMR ((D₇)DMF): 10.40 (*s*, NH); 8.40 (*d*, *J* = 8.1, 1 arom. H); 8.21 (*d*, *J* = 8.5, 2 arom. H); 7.94 (*d*, *J* = 8.1, 1 arom. H); 7.69 (*t*-like, 2 arom. H); 7.61 (*d*-like, 2 arom. H); 5.03 (*q*, *J* = 7.0, CH₂); 4.11 (*s*, MeO); 1.60 (*t*, *J* = 7.0, MeCH₂). ¹³C-NMR ((D₇)DMF): 162.7 (*s*, CO)³; 153.1, 148.6, 148.5, 140.9, 136.0, 131.2, 119.0, 117.6, 115.2, 105.8 (10_s, 10 arom. C); 132.3, 129.9, 129.1, 126.5,

²) In all Se-containing products, the values for C were too low.

³) Signal overlaps with the signal of DMF.

123.4, 121.9 (6d, 8 arom. CH); 52.2 (q, MeO); 42.9 (t, CH₂); 15.9 (q, MeCH₂). CI-MS: 529 (100, [M+1]⁺). Anal. calc. for C₂₂H₁₇BrN₄O₂Se (528.26): C 50.02, H 3.24, N 10.61; found C 49.33, H 3.43, N 10.50.

Methyl *1-Ethyl-4-[(4-methoxyphenyl)amino]-1H-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate (9d)*. From 0.4 g (1.31 mmol) of **6** and 0.36 g (1.69 mmol) of **8d**. Yield: 0.5 g (79.4%). Yellowish crystals. M.p. 249.2 – 250.0° (CH₂Cl₂/hexane). IR: 3262w, 3198w, 3123w, 3062m, 2988m, 2949m, 2833w, 1692s, 1601s, 1569s, 1535m, 1508s, 1476m, 1460m, 1438m, 1414m, 1372m, 1354m, 1297m, 1279w, 1241s, 1218s, 1197m, 1179w, 1161m, 1136w, 1110m. ¹H-NMR (500 MHz, (D₆)DMSO): 10.06 (s, NH); 8.30 (br. d, J = 8.0, 1 arom. H); 8.00 (br. d, J = 8.8, 2 arom. H); 7.89 (dd, J = 8.2, 1.2, 1 arom. H); 7.66 (td, J = 8.2, 1.2, 1 arom. H); 7.58 (td, J = 8.2, 1.2, 1 arom. H); 6.94 (d-like, J = 9.1, 2 arom. H); 4.93 (q, J = 7.0, CH₂); 3.97, 3.77 (2s, 2 MeO); 1.50 (t, J = 7.0, MeCH₂). ¹³C-NMR ((D₆)DMSO): 161.3 (s, CO); 154.9, 152.4, 147.1, 135.6, 133.7, 131.0, 128.4, 115.9, 104.6 (9s, 10 arom. C); 128.5, 125.8, 122.5, 120.5, 117.7, 113.7 (6d, 8 arom. CH); 55.2, 51.6 (2q, 2 MeO); 41.8 (t, CH₂); 15.3 (q, MeCH₂). CI-MS: 481 (100, [M+1]⁺). Anal. calc. for C₂₃H₂₀N₄O₃Se (479.39): C 57.62, H 4.21, N 11.69; found C 55.90, H 4.22, N 11.32.

Methyl *4-[(4-Chlorophenyl)(methyl)amino]-1-ethyl-1H-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate (10)*. To a soln. of **9b** (0.2 g, 0.4 mmol) in dry pyridine (30 ml) was added a suspension of NaH in mineral oil (ca. 1.5 eq.) and 1.2 eq. CH₃I. Usual workup and crystallization yielded 0.1 g (50%) of **10**. Creamy-colored crystals. M.p. 215.1 – 215.5° (CH₂Cl₂/hexane). IR: 3181w, 3048w, 2927m, 1695s, 1611m, 1596s, 1584s, 1567s, 1552s, 1489s, 1461s, 1435s, 1405m, 1373s, 1350m, 1314s, 1285s, 1263m, 1243m, 1222s, 1191s, 1158m, 1127m, 1110s, 1090m. ¹H-NMR ((D₇)DMF): 8.37 (d, J = 8.3, 1 arom. H); 8.35 (d-like, 1 arom. H); 7.88 (d-like, 2 arom. H);

7.85 – 7.49 (*m*, 4 arom. H); 5.00 (*q*, *J* = 6.8, CH₂); 3.97 (*s*, MeO); 3.63 (*s*, MeN); 1.57 (*t*, *J* = 7.0, MeCH₂). CI-MS: 499 (100, [M+1]⁺).

4. *Preparation of Methyl 4-[(4-Bromophenyl)amino]-1-ethyl-1H-5-thia-1,3,6-triazaceanthrylene-4-carboxylate (12)*. In analogy to the *General Procedure* (section 3), **12** was prepared from 0.4 g (1.32 mmol) of **6** and 0.29 g (1.35 mmol) of (4-bromophenyl) isothiocyanate. Yield: 0.4 g (63.5%). Pale yellow crystals. M.p. 286.1 – 286.5° (MeOH). IR: 3416*w*, 3305*s*, 3194*m*, 3120*m*, 3054*w*, 2946*w*, 2926*w*, 2852*w*, 1662*s*, 1601*s*, 1562*s*, 1540*s*, 1487*s*, 1468*s*, 1439*m*, 1395*m*, 1378*m*, 1353*w*, 1308*s*, 1293*m*, 1261*m*, 1249*w*, 1223*s*, 1199*m*, 1179*m*, 1157*m*, 1132*m*, 1116*m*. ¹H-NMR ((D₇)DMF)⁴: 12.93 (*s*, 0.33 NH); 10.43 (*s*, 0.66 NH); 8.61 – 8.59 (*d*-like, 0.33 arom. H); 8.39 – 8.37 (*d*-like, 0.66 arom. H); 8.24 – 8.22 (*m*, 2 arom. H); 7.93 – 7.92 (*d*-like, 0.33 arom. H); 7.89 – 7.88 (*d*-like, 0.66 arom. H); 7.70 – 7.53 (*m*, 4 arom. H); 5.04 (*q*, *J* = 7, CH₂); 4.09, 4.04 (2*s*, MeO); 1.59 (*t*, *J* = 7, MeCH₂). ¹³C-NMR ((D₇)DMF)⁴: 162.4, 162.0 (2*s*, CO); 153.0, 151.6, 151.1, 148.5, 148.0, 140.8, 135.1, 132.8, 132.6, 119.2, 119.1, 116.1, 115.3, 107.1, 10.2 (15*s*, 10 arom. C); 132.3, 132.2, 129.9, 129.4, 129.2, 126.5, 126.2, 123.6, 123.4, 122.3, 122.2 (11*d*, 8 arom. CH); 52.0, 51.9 (2*q*, MeO); 42.8 (*t*, CH₂); 15.9 (*q*, MeCH₂). CI-MS: 483 (100, [M+1]⁺). Anal. calc. for C₂₂H₁₇BrN₄O₂S (481.36): C 54.89, H 3.56, N 11.64; found: C 54.06, H 3.68, N 11.54.

⁴) Two tautomeric forms of **12** are present in a ratio of *ca.* 1 : 2. Some of the signals overlap.

5. *X-Ray Crystal-Structure Determination of 9c and 12 (Table and Figs. 1 and 2)*⁵). All measurements were made on a *Nonius KappaCCD* diffractometer [25] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1* and *2*. Data reductions were performed with *HKL Denzo* and *Scalepack* [26]. The intensities were corrected for *Lorentz* and polarization effects, and, in the case of **9c**, a numerical absorption correction [27] was applied, whereas in the case of **12**, an absorption correction based on the multi-scan method [28] was applied. The structures were solved by direct methods using *SIR92* [29], which revealed the positions of all non-H-atoms. In the case of **12**, the asymmetric unit contains one molecule of **12** plus one molecule of DMSO. The non-H-atoms were refined anisotropically. In both structures, the NH-atom was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent C-atom (1.5U_{eq} for the Me groups). Refinements of the structures were carried out on F^2 using full-matrix least-squares procedures, which minimised the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in both cases. Neutral atom scattering factors for non-H-atoms were taken from [30a], and the scattering factors for H-atoms were

⁵) CCDC-211324 & 211325 contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

taken from [31]. Anomalous dispersion effects were included in F_c [32]; the values for f' and f'' were those of [30b]. The values of the mass attenuation coefficients are those of [30c]. All calculations were performed using the *SHELXL97* program [33].

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Legends

Fig. 1. *ORTEP-Plot* [20] of the molecular structure of **9c** (arbitrary numbering of atoms; 50% probability ellipsoids)

Fig. 2. *ORTEP-Plot* [20] of the molecular structure of **12** (arbitrary numbering of atoms; 50% probability ellipsoids)